

DRYING OF BEULAH-ZAP LIGNITE.  
PRETREATMENT WITH SOLVENTS AND REHYDRATION

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Keywords: Drying, Solvent pretreatment, Rehydration

ABSTRACT

Lignite (-100 mesh from the Argonne Premium Coal Sample Program) was dried in nitrogen under various conditions in a Cahn 121 thermobalance as part of a program on drying low rank coals for liquefaction. Samples were pretreated with solvents to determine the solvent's ability to displace water from the pores. Toluene had little effect. Acetone and methanol, selected because of water miscibility, were examined also. The methanol accelerated the drying, apparently because it was able to diffuse into the pores. The effect of drying on reactivity was examined by determining the rate of rehydration. Hysteresis was also examined. Rehydration is slow, and incomplete within a 23 hour period. The ability of carbon dioxide to substitute for nitrogen was examined. The behavior was similar with slight advantages for using nitrogen.

INTRODUCTION

Liquefaction of coals at low severity conditions is an important goal of coal research to maintain an economical, stable, long term supply of liquid fuels. Lignite is an abundant and reactive U. S. coal. One of the detracting properties of lignite is the high moisture content. Drying is usually carried out to minimize the impact of this constituent in the conversion process. Drying affects the reactivity of the coal. This effect is thought to be due to physical changes, such as irreversible pore collapse and/or other structural changes. Earlier work has indicated changes in the oil yield derived from raw, partly dried and more completely dried lignite samples (1).

Comments by some speakers to the effect that carbon dioxide can more effectively displace moisture from coal than nitrogen, reminiscent of use for surface area measurements or oil displacement from source rock, led to tests of the substitution of carbon dioxide for nitrogen in drying experiments.

It has also been suggested that the use of light oil to agglomerate coal prior to liquefaction may be beneficial in terms of moisture removal. There are benefits in terms of mineral reduction. Some added experiments were carried out to determine the capability of a light aromatic hydrocarbon and some other small hydrophilic molecules to accelerate drying rates.

The reactivity of the product coal is always of concern. A loss in reactivity due to a drying method, even though drying is improved, may preclude the use of the drying method. A standard

test adopted here for comparison of reactivity has been the ability to rehydrate the sample, as measured by the rate under a standard set of conditions.

#### EXPERIMENTAL

Coal drying was done with a Cahn model 121 thermobalance attached to an IBM PC/XT microcomputer. Vendor-supplied software was used to monitor the progress of individual runs, and convert data files to a form that could be further studied with Lotus 123.

The data were obtained as files of time, temperature and weight at 10 second intervals. Run times varied from 7-23 hours. Sample sizes started as about 80 mg. Temperatures were 30 or 40 C. The gas velocity past the sample was typically 80 cc/min in the 25 mm diameter tube. The sample was placed in a quartz flat bottom pan. The sample was the -100 mesh Argonne Premium Coal Sample - Beulah-Zap lignite (5).

Samples were quickly transferred from ampoules which had been kept in constant humidity chambers with water at room temperature (293°K). In the thermobalance system a period of about 5 minutes was used to stabilize the system and initiate data acquisition. A condenser was made to replace the usual quartz envelope that surrounds the sample. An antifreeze solution was circulated from a constant temperature bath through the condenser to maintain constant temperature during the experiments. This was more stable than the original furnace and provided very uniform temperature control during the experiments.

The gas atmosphere for the nitrogen gas runs was cylinder nitrogen (99.99%) or "house" nitrogen from the evaporation of liquid nitrogen storage containers used without further purification. For the carbon dioxide the gas was 99.9% carbon dioxide from a gas cylinder. The gas velocity was measured with a float-type flowmeter and adjusted for the density difference between carbon dioxide and air.

Data were analyzed as reported earlier (1,2,3,4). The best fit was obtained with a first order or unimolecular expression. Regression analysis was used to obtain the kinetic constants. Lotus 123 was used for analysis of individual run data. Approximations to a first and second derivative of the rate expressions were made in Lotus 123 by averaging over 20 of the 10 second time intervals before and after the point of interest. These derivatives were plotted with the rate data for further interpretation of the data.

Experiments with solvents were carried out by weighing the samples as usual and then adding solvent so that the sample was just covered with liquid. This was done on a balance to determine the amounts of solvent. The sample was then transferred to the TGA and a drying run was carried out in nitrogen as with earlier samples. There was about five minutes of contact time before the beginning of the drying run.

The reactivity of the sample was checked by measuring the rate of hydration. Tests of rehydration or humidification involved switching the gas atmosphere by passing the same gas flow through a coarse fritted gas bubbler filled with distilled water at room temperature (293°K). Typical times for the change were about 5 minutes. Finally hysteresis checks were made by redrying the humidified sample following the procedure for the initial drying.

## RESULTS AND DISCUSSION

Earlier work by the author with higher rank coal samples (3,4) included studies of humidification of dried samples to determine hysteresis, observe consistency or changes in mechanism of reaction and compare rates of moisture loss and gain.

### Basis for Comparison

The solvent based runs were carried out at 30°C and the runs with carbon dioxide were carried out at 40°C and a gas flow rate of 80 cc/min with sample sizes of about 80 mg. Runs with nitrogen at those conditions were used for comparison. The sets of runs include 135-7, 145-146, 150-2.

In this series of runs the sample was initially dried in nitrogen, then the gas atmosphere was changed to humid nitrogen to allow humidification to take place, and then the sample was redried to compare with the original drying. Three series of runs are summarized in Table 1.

Table 1. Runs in Nitrogen for Comparison

Run #	Coal type	$k_1$ dry	Moisture	$k_{\text{humid}}$	$k_{\text{redry}}$	Temp
135-7	raw	.00269	31.86%	.00264	not run	30 C
145-6	equil	.00323	29.6%	.00445	not run	30 C
150-2	equil	.00503	32.25%	.0092	.00367	40 C

MC?

A typical run series in which the three runs are superimposed is shown in Figure 1. The runs indicate that the raw coal (fresh from the ampoule) does not lose moisture as rapidly as the sample which has been allowed to equilibrate with water in a desiccator chamber at room temperature for at least a few days. Under similar conditions the equilibrated coal does not lose as much moisture as the fresh one. The rate of hydration of the equilibrated coal is greater than the rate for the raw coal. The indicated rate reflects the speed of approach to the final state for the system. The final state for rehydration or humidification involves a significantly lower moisture content than the starting material (i.e. 5% vs 31%). Therefore a comparison, per unit time, of the mass of water initially lost with the amount regained by the coal indicates that the rate of loss in the initial drying surpasses the rate of rehydration by a significant amount.

The rate of humidification of the dried coal from experiments at 40 C increases more than the rate of drying compared to the rates at 30 C. The shape of the rate function versus time curve is different for the redrying of the humidified coal than for the

original drying of the coal, implying a change, probably to a desorption mechanism. A slightly higher amount of moisture is removed by drying at higher temperature.

#### Drying in Carbon Dioxide

Two samples (about 80 mg) were each placed through a series of three runs without removing them from the TGA. The purpose was to establish the drying rate, rehydration rate and hysteresis by measuring the redrying rate of the humidified sample (one was at 57 cc/min gas flow, while the other was at 80 cc/min). These rates were to be compared to those in nitrogen.

A comparison of the data with that indicated above using nitrogen indicated that the drying behavior in carbon dioxide is very similar. The CO<sub>2</sub> drying rate (run 166) was .00398 based on mg water/gm sample per 10 second interval at 40°C with a gas flow rate of 57 cc/min. The weight loss amounted to 30.12% moisture removal. The indicated rate followed an induction period of about 1800 seconds while the rate slowly increased from .00333 to .00398. Following the initial 4,200 seconds of the run the rate gradually slowed so that in the period from 28,000 to 44,000 seconds the rate was .00056 based on mg water/gm sample/10 second interval. The rate slowed even further after that and the run was ended after 68,040 seconds.

Following a five minute changeover to humid CO<sub>2</sub>, data on hydration were obtained. The rate of hydration (run 167) following drying in carbon dioxide also followed a first order expression. About 200 seconds were needed for the moist carbon dioxide to displace the dry gas. The rate gradually increased over about 1600 seconds until it became constant at about .00521 mg water/gm sample/10 second interval at the 57 cc/min flow rate. After 3600 seconds the rate gradually decreased. It should be noted that the rate of rehydration was greater than the rate of drying. The moisture addition resulted in restoration of the moisture content to only 4.45% compared to 30.1% originally.

The humidified sample was redried in run 168 to compare the behavior with the raw sample and establish hysteresis effects. The weight loss data no longer followed a first order expression, so a direct comparison of rates was not possible. The data appear to be closer to a desorption kinetic form, indicating a significant change in mechanism. Figure 2 shows the weight change data for the three runs.

Another sample was run through the same three steps of drying, rehydration and redrying to check the reproducibility of results and compare the behavior at 80 cc/min gas flow. Runs 169-171 showed the same behavior and the weight curves superimpose very well.

When the gas flow rate was 80 cc/min the drying rate increased from .00326 to .00403. The duration of the interval for the high rate was about 3,300 seconds and then the rate gradually decreased to .00177, about three times the rate for run 166.

The rate constant for humidification in run 170 at 80 cc/min was initially .0053 and increased to .0062.

The redrying of the humidified sample in run 171 indicated that the mechanism has again shifted as the rate constantly decreased if a first order plot was attempted. Again, desorption kinetics seem more appropriate.

The initial changes in the rate during the first drying prompted a re-examination of a number of runs to determine if the rate change might be due to some induction step or thermal lag as the sample changed temperature or possibly induced by the gas flow. Runs 135 at 30°C in nitrogen and 150 at 40°C in nitrogen were studied for this purpose. Each of these involved sample sizes of about 80 mg with the same flat bottom quartz bucket and 80 cc/min gas flow past the sample.

A superposition of Figures 1 and 2 indicates that similar runs in nitrogen show a more rapid loss of moisture.

#### Drying with Solvents

Several solvents were used to explore the effects of treatment with volatile hydrocarbons and water miscible solvents (toluene, acetone and methanol). A run using water in place of a solvent was carried out for a check on the experimental procedure. The experimental results are indicated in Table 2.

The rates of drying for the toluene treated sample appear to be less than that for the others. Treatment with acetone is essentially similar to the base water case. Treatment with water appears to cause a slight increase. The addition of methanol apparently permits diffusion of the miscible solvent into the pores such that the measured mass change is accelerated. The change can be due to a combination of a real rate increase and the increase in mass of methanol compared to water (neglecting volume effects).

The solvents rapidly evaporated following a linear weight loss with time. The drying then appeared to be similar to normal drying in mechanism and in terms of rates, except as noted above. Humidification and redrying were similar also to the cases of nitrogen drying of normal samples.

Table 2. Drying Lignite After Exposure to Solvents at 30°C

Solvent	Run #	$k_1$ dry	Moisture
Toluene	137-9	.00317	29.0%
Acetone	140-2	.00333	30.3%
Methanol	142-4	.00397	31.1%
Water	147-8	.00363	30.4%

#### Drying in Humid Nitrogen

A series of runs were carried out in humid nitrogen to determine the limits of water reabsorption, and search for changes in rate or mechanism. Runs 154-5 at 40°C and 156 at 60°C are summarized in Table 3.

Table 3. Drying Lignite in Humid Nitrogen

Run #	Temp°C	k <sub>humid</sub>	Moisture Loss	k <sub>dry N</sub>	k <sub>humid 2</sub>
154	40	.00414	23.7%		
156	60	.01227	28.5%	.00531	.01736

It is no surprise that the rates of drying are less than those under dry conditions, in this case about 80% of the rate at 40°C. The amount of moisture lost at 40°C is about 7-8% less than that lost using dry nitrogen.

#### CONCLUSIONS

A base set of rates is available to compare the results of thermogravimetric analysis (TGA) experiments over the temperature range of interest.

The curves for drying and humidification with moist nitrogen or carbon dioxide are very similar.

The curves for redrying humidified samples are different from the drying of the original sample, implying a different mechanism for the second moisture loss, probably following a desorption rate control.

The use of solvents to accelerate the rate of drying does not seem to be beneficial with a non-miscible aromatic light hydrocarbon like toluene. A water miscible solvent like acetone was not beneficial either when the contact time before the experiment was only five minutes. A smaller water miscible molecule did have an effect, indicating that the rate would increase.

The use of humid nitrogen in place of nitrogen reduces the amount of moisture that will be removed in an initial drying. The amount that can be restored in humidification at a given temperature is also reduced indicating a limited reactivity compared to a nitrogen dried material.

#### ACKNOWLEDGMENTS

The author gratefully acknowledges the support of the U. S. Department of Energy, Pittsburgh Energy Technology Center.

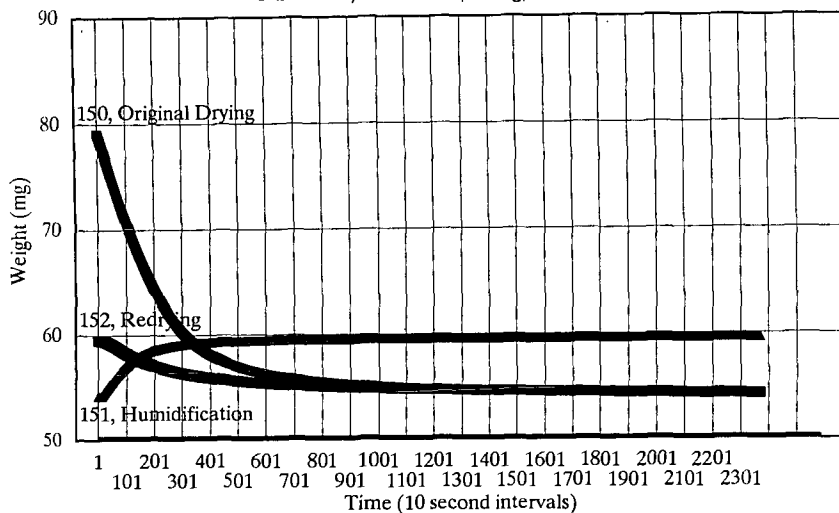
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# Fig. 1, Lignite in N2, 40 C

ND150-2, -100 mesh, 81 mg, 80 cc/min, fbb



# Fig. 2, Lignite in CO2, 40 C

ND166-68, -100 mesh, 83 mg, 57 cc/min, fbb

